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(57) Abstract

A process for extinguishing, preventing and/or controlling fires using a composition containing CHF_3 is disclosed. CHF_3 can be used in volume percentages with air as high as 80 % without adversely affecting mammalian habitation, with no effect on the ozone in the stratosphere and with little effect on the global warming process.

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Fire Extinguishing Composition and Process

CROSS REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of U. S. Application Serial No. 07/417,654, filed on October 4, 1989.

Field of Invention

This invention relates to compositions for use in preventing and extinguishing fires based on the combustion of combustible materials. More particularly, it relates to such compositions that are "safe" to use -- as safe for humans as currently used extinguishants but absolutely safe for the environment. Specifically, the compositions of this invention have little or no effect on the ozone layer depletion process; and make no or very little contribution to the global warming process known as the "greenhouse effect". Although these compositions have minimal effect in these areas, they are extremely effective in preventing and extinguishing fires, particularly fires in enclosed spaces.

Background of the Invention and Prior Art

In preventing or extinguishing fires, two important elements must be considered for success: (1) separating the combustibles from air; and (2) avoiding or reducing the temperature necessary for combustion to proceed. Thus, one can smother small fires with blankets or with foams to cover the burning surfaces to isolate the combustibles from the oxygen in the air. In the customary process of pouring water on the burning surfaces to put out the fire, the main element is reducing temperature to a point where

combustion cannot proceed. Obviously, some smothering or separation of combustibles from air also occurs in the water situation.

The particular process used to extinguish fires depends upon several items, e.g. the location of the fire, the combustibles involved, the size of the fire, etc. In fixed enclosures such as computer rooms, storage vaults, rare book library rooms, petroleum pipeline pumping stations and the like, halogenated hydrocarbon fire extinguishing agents are currently preferred. These halogenated hydrocarbon fire extinguishing agents are not only effective for such fires, but also cause little, if any, damage to the room or its contents. This contrasts to the well-known "water damage" that can sometimes exceed the fire damage when the customary water pouring process is used.

The halogenated hydrocarbon fire extinguishing agents that are currently most popular are the bromine-containing halocarbons, e.g. bromotrifluoromethane (CF_3Br, Halon 1301) and bromochlorodifluoromethane (CF_2ClBr, Halon 1211). It is believed that these bromine-containing fire extinguishing agents are highly effective in extinguishing fires in progress because, at the elevated temperatures involved in the combustion, these compounds decompose to form products containing bromine atoms which effectively interfere with the self-sustaining free radical combustion process and, thereby, extinguish the fire. These bromine-containing halocarbons may be dispensed from portable equipment or from an automatic room flooding system activated by a fire detector.

In many situations, enclosed spaces are involved. Thus, fires may occur in rooms, vaults,

enclosed machines, ovens, containers, storage tanks, bins and like areas. The use of an effective amount of fire extinguishing agent in an atmosphere which would also permit human occupancy in the enclosed space involves two situations. In one situation, the fire extinguishing agent is introduced into the enclosed space to extinguish an existing fire; the second situation is to provide an ever-present atmosphere containing the fire "extinguishing" or, more accurately, the fire prevention agent in such an amount that fire cannot be initiated nor sustained. Thus, in U.S. Patent 3,844,354, Larsen suggests the use of chloropentafluoroethane (CF_3-CF_2Cl) in a total flooding system (TFS) to extinguish fires in a fixed enclosure, the chloropentafluoroethane being introduced into the fixed enclosure to maintain its concentration at less than 15%. On the other hand, in U.S. Patent 3,715,438, Huggett discloses creating an atmosphere in a fixed enclosure which is habitable but, at the same time, does not sustain combustion. Huggett provides an atmosphere consisting essentially of air, a perfluorocarbon selected from carbon tetrafluoride, hexafluoroethane, octafluoropropane and mixtures thereof and make-up oxygen, as required.

It has also been known that bromine-containing halocarbons such as Halon 1301 can be used to provide a habitable atmosphere that will not support combustion. However, the high cost due to bromine content and the toxicity to humans i.e. cardiac sensitization at relatively low levels (e.g. Halon 1301 cannot be used above 7.5-10%) make the bromine-containing materials unattractive for long term use.

In recent years, even more serious objections to the use of brominated halocarbon fire extinguishants has arisen. The depletion of the stratospheric ozone

layer, and particularly the role of chlorofluorocarbons (CFC's) have led to great interest in developing alternative refrigerants, solvents, blowing agents, etc. It is now believed that bromine-containing halocarbons such as Halon 1301 and Halon 1211 are at least as active as chlorofluorocarbons in the ozone layer depletion process.

While perfluorocarbons such as those suggested by Huggett, cited above, are believed not to have as much effect upon the ozone depletion process as chlorofluorocarbons, their extraordinarily high stability makes them suspect in another environmental area, that of "greenhouse effect". This effect is caused by accumulation of gases that provide a shield against heat transfer and results in the undesirable warming of the earth's surface.

There is, therefore, a need for an effective fire extinguishing composition and process which can also provide safe human habitation and which composition contributes little or nothing to the stratospheric ozone depletion process or to the "greenhouse effect".

It is an object of the present invention to provide such a fire extinguishing composition; and to provide a process for preventing and controlling fire in a fixed enclosure by introducing into said fixed enclosure, an effective amount of the composition.

Summary of Invention

The present invention is based on the finding that an effective amount of a composition consisting essentially of at least one fluoro-partially substituted ethane selected from the group of pentafluoroethane (CF_3-CHF_2), also known as FC-125, and the tetrafluoroethanes (CHF_2-CHF_2 and CF_3-CH_2F), also

known as FC-134 and FC-134a, will prevent and/or extinguish fire based on the combustion of combustible materials, particularly in an enclosed space, without adversely affecting the atmosphere from the standpoint of toxicity to humans, ozone depletion or "greenhouse effect".

The trifluoromethane may be used in conjunction with as little as 1% of at least one halogenated hydrocarbon selected from the group of difluoromethane (HFC-32), chlorodifluoromethane (HCFC-22), 2,2-dichloro-1,1,1-trifluoroethane HCFC-123), 1,2-dichloro-1,1,2-trifluoroethane (HCFC-123a), 2-chloro-1,1,1,2-tetrafluoroethane (HCFC-124), 1-chloro-1,1,2,2-tetrafluoroethane (HCFC-124a), pentafluoroethane (HFC-125), 1,1,2,2-tetrafluoroethane (HFC-134), 1,1,1,2-tetrafluoroethane (HFC-134a), 3,3-dichloro-1,1,1,2,2-pentafluoropropane (HCFC-225ca), 1,3-dichloro-1,1,2,2,3-pentafluoropropane (HCFC-225cb), 2,2-dichloro-1,1,1,3,3-pentafluoropropane (HCFC-225aa), 2,3-dichlorol,1,1,3,3-pentafluoropropane (HCFC-225da), 1,1,1,2,2,3,3-heptafluoropropane (HFC-227ca), 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea), 1,1,1,2,3,3-hexafluoropropane (HFC-236ea), 1,1,1,3,3,3-hexafluoropropane (HFC-236fa), 1,1,1,2,2,3-hexafluoropropane (HFC-236cb), 1,1,2,2,3,3-hexafluoropropane (HFC-236ca), 3-chloro-1,1,2,2,3-pentafluoropropane (HCFC-235ca), 3-chloro-1,1,1,2,2-pentafluoropropane (HCFC-235cb), 1-chloro-1,1,2,2,3-pentafluoropropane (HCFC-235cc), 3-chloro-1,1,1,3,3-pentafluoropropane (HCFC-235fa), 3-chloro 1,1,1,2,2,3-hexafluoropropane (HCFC-226ca), 1-chloro-1,1,2,2,3,3-hexafluoropropane (HCFC-226cb),

2-chloro-1,1,1,3,3,3-hexafluoropropane (HCFC-226da), 3-chloro-1,1,1,2,3,3-hexafluoropropane (HCFC-226ea), and 2-chloro-1,1,1,2,3,3-hexafluoropropane (HCFC-226ba)

One particularly surprisingly effective application of the invention is its use in providing a habitable atmosphere, as defined in Huggett U.S. Patent No. 3,715,438. Thus, the invention would comprise a habitable atmosphere, which does not sustain combustion of combustible materials of the non-self-sustaining type, i.e. a material which does not contain an oxidizer component capable of supporting combustion, and which is capable of sustaining mammalian life, consisting essentially of (a) air; (b) the fluoroethane (FC125, 134 and/or 134a) in an amount sufficient to suppress combustion of the combustible materials present in an enclosed compartment containing said atmosphere; and, optionally if necessary, (c) make-up oxygen in an amount from zero to the amount required to provide, together with the oxygen in the air, sufficient total oxygen to sustain mammalian life.

The invention also comprises a process for preventing and controlling fire in an enclosed air-containing mammalian-habitable compartment which contains combustible materials of the non self-containing type which consists essentially of:
(a) introducing at least one of the aforementioned fluoroethanes into the air in the enclosed compartment in an amount sufficient to suppress combustion of the combustible materials in the enclosed compartment; and
(b) introducing oxygen in an amount from zero to the amount required to provide, together with the oxygen present in the air, sufficient total oxygen to sustain mammalian life.

Preferred Embodiments

The tri-fluoroalkane, CHF_3, when added in adequate amounts to the air in a confined space, eliminates the combustion-sustaining properties of the air and suppresses the combustion of flammable materials, such as paper, cloth, wood, flammable liquids, and plastic items, which may be present in the enclosed compartment, without detriment to normal mammalian activities.

Tri-fluoromethane is extremely stable and chemically inert. CHF_3 does not decompose at temperatures as high as 400°C to produce corrosive or toxic products and cannot be ignited even in pure oxygen so that they continue to be effective as a flame suppressant at the ignition temperatures of the combustible items present in the compartment. CHF_3 is also physiologically inert.

Tri-fluoromethane is additionally advantageous because of its low boiling points, i.e. a boiling point at normal atmospheric pressure of 82.1°C. Thus, at any low environmental temperature likely to be encountered, this gas will not liquefy and will not, thereby, diminish the fire preventive properties of the modified air. In fact, any material having such a low boiling point would be suitable as a refrigerant.

Tri-fluoromethane is also characterized by an extremely low boiling point and a high vapor pressure, i.e. about 635 psig at 21°C. This permits CHF_3 to act as its own propellant in "hand-held" fire extinguishers. It may also be used with other materials such as those disclosed on pages 5 and 6 of this specification to act as the propellant and co-extinguishant for these materials of lower vapor pressure. Its lack of toxicity (comparable to

nitrogen) and its short atmospheric lifetime (with little effect on the global warming potential) compared to the perfluoroalkanes (with lifetimes of over 500 years) make CHF_3 ideal for this portable fire-extinguisher use.

As the propellant in a hand-held or other portable platform system (wheeled unit, truck-mounted unit, etc.) the trifluoromethane may comprise anywhere from 0.5 weight percent to 99 weight percent of the mixture with one or more of the compounds listed on pages 5 and 6. When it acts as its own propellant, of course, it comprises 100% of the propellant-extinguisher mixture.

To eliminate the combustion-sustaining properties of the air in the confined space situation, the gas should be added in an amount which will impart to the modified air a heat capacity per mole of total oxygen present, including any make-up oxygen required, sufficient to suppress or prevent combustion of the flammable, non-self-sustaining materials present in the enclosed environment. Surprisingly, we have found that with the use of CHF_3, the quantity of CHF_3 required to suppress combustion is sufficiently low as to eliminate the requirement for make-up oxygen.

The minimum heat capacity required to suppress combustion varies with the combustibility of the particular flammable materials present in the confined space. It is well known that the combustibility of materials, namely their capability for igniting and maintaining sustained combustion under a given set of environmental conditions, varies according to chemical composition and certain physical properties, such as surface area relative to volume,

heat capacity, porosity, and the like. Thus, thin, porous paper such as tissue paper is considerably more combustible than a block of wood.

In general, a heat capacity of about 40 cal./°C and constant pressure per mole of oxygen is more than adequate to prevent or suppress the combustion of materials of relatively moderate combustibility, such as wood and plastics. More combustible materials, such as paper, cloth, and some volatile flammable liquids, generally require that the CHF_3 be added in an amount sufficient to impart a higher heat capacity. It is also desirable to provide an extra margin of safety by imparting a heat capacity in excess of minimum requirements for the particular flammable materials. A minimum heat capacity of 45 cal./°C per mole of oxygen is generally adequate for moderately combustible materials and a minimum of about 50 cal./°C per mole of oxygen for highly flammable materials. More can be added if desired but, in general, an amount imparting a heat capacity higher than about 55 cal./°C per mole of total oxygen adds substantially to the cost and may create unnecessary physical discomfort without any substantial further increase in the fire safety factor.

Heat capacity per mole of total oxygen can be determined by the formula:

$$C_p^* = (C_p)_{O_2} + \sum_z \frac{P_z}{P_{O_2}} (C_p)_z$$

wherein:

C_p^* = total heat capacity per mole of oxygen at constant pressure;

P_{O_2} = partial pressure of oxygen;

P_z = partial pressure of other gas;

$(C_p)_z$ = heat capacity of other gas at constant pressure.

The boiling points of CHF_3 and the mole percent required to impart to air heat capacities (C_p) of 40 and 50 cal./°C at a temperature of 25°C and constant pressure while maintaining a 21% oxygen content are tabulated below:

	Boiling point, °C.	C_p=40 percent	C_p=50 percent
CHF_3	-82.1	21.5	62.0

It will be noted from Example 2 that CHF_3 is not toxic at concentration up to about 80%.

The concentration of oxygen available in the confined air space should be sufficient to sustain mammalian life. The amount of make-up oxygen, if required, is determined by such factors as degree of air dilution by the CHF_3 gas and depletion of the available oxygen in the air by human respiration. The amount of oxygen required to sustain human, and therefore mammalian life in general, at atmospheric, subatmospheric, and superatmospheric pressures, is well known and the necessary data are readily available. See, for example, Paul Webb, Bioastronautics Data Book, NASA SP-3006, National Aeronautics and Space Administration, 1964, p. 5. The minimum oxygen partial pressure is considered to be about 1.8 p.s.i.a., with amounts above 8.2 p.s.i.a. causing oxygen toxicity. At normal atmospheric pressures at sea level, the unimpaired performance zone is in the range of about 16

to 36 volume percent of oxygen. The normal amount of oxygen maintained in a confined space is about 16% to about 21% at normal atmospheric pressure.

In most applications using CHF_3, no make-up oxygen will be required initially or even thereafter, since the CHF_3 volume requirement even when the starting oxygen amount of 21% decreased to 16%, is extremely small. However, habitation for extended periods of time will generally require addition of oxygen to make up the depletion caused by respiration.

Introduction of the CHF_3 gas and any oxygen is easily provided for by metering appropriate quantities of the gas or gases into the enclosed air-containing compartment.

The air in the compartment can be treated at any time that it appears desirable. The modified air can be used continuously if a threat of fire is constantly present or the particular environment is such that fire hazard must be kept at an absolute minimum, or it can be used as an emergency measure if a threat of fire develops.

As stated previously, small amounts of one or more of the compounds set forth on pages 5 and 6 may be used along with the CHF_3 gas without upsetting the mammalian habitability or losing the other advantages of the CHF_3.

The invention will be more clearly understood by referring to the examples which follow. The unexpected effects of CHF_3, and CHF_3 in the aforementioned blends, in suppressing and combatting fire, as well as its compatability with the ozone layer and its relatively low "greenhouse effect", when compared to other fire-combatting gases, particularly the perfluoroalkanes, are shown in the examples.

Example 5 CHF_3 as a Propellant
(compared to nitrogen)

The discharge properties of 2,2-dichloro-1,1,1-trifluoroethane were measured first pressurized with nitrogen as a control example and then pressurized with trifluoromethane as Example 5.

Control - 1182.2 grams of 2,2-dichloro-1,1,1-trifluoroethane (HCFC-123) was added to a container serving as an extinguisher. The container was then pressurized to 151 psig with 5.3 grams of nitrogen. Then, the extinguisher contained 99.5% HCFC-123 and 0.5% nitrogen.

Example - 1014 grams of HCFC-123 was added to a container serving as an extinguisher. The container was then pressurized to 150 psig (equivalent to the Control) with 108.5 grams of CHF_3. Thus, the extinguisher contained 90.3% HCFC-123 and 9.7% CHF_3.

Both extinguishers were discharged in short bursts and the reduced pressures between bursts recorded in Tables 5 and 5A. It will be noted that the pressure was lost very rapidly in the Control example even with only 12.5 wt.% of the contents discharged; whereas the propellant (CHF_3) in Example 5 maintains over 67% of the original pressure even after almost 87 wt.% of the contents have been discharged. Compare the 21st burst in Table 5 to the first burst in Table 5A.

Although this example discloses the use of CHF_3 as a propellant for portable fire extinguishers at an initial pressure of 150 psig (approximately 10.5 bars), it should be understood that lower pressures can be used. Thus, at room temperature (20°C), it would not be advisable to pressurize the extinguisher with CHF_3 above 2.5 bars for a glass container, nor above 4.5 bars for one composed of tin.

It is also understood that, although the starting weight percent of the CHF_3 propellant in the example was about 10%, anywhere from 0.5 to 100 weight percent of CHF_3 may be used in this invention.

TABLE 5

Burst	Total Wt. (gms)	Weight Change (gms)	Discharge (%)	Pressure (psig)	Pressure Change (psig)
0	2798.8		-0.0	150.0	
1	2753.5	45.3	4.0	148.0	2.0
2	2713.0	40.5	7.6	146.0	2.0
3	2669.3	43.7	11.5	145.0	1.0
4	2624.5	44.8	15.5	144.0	1.0
5	2575.3	49.2	19.9	142.0	2.0
6	2528.9	46.4	24.0	140.0	2.0
7	2487.4	41.5	27.7	138.0	2.0
8	2448.3	39.1	31.2	136.0	2.0
9	2390.5	57.8	36.4	134.0	2.0
10	2348.1	42.4	40.2	133.0	1.0
11	2304.0	44.1	44.1	130.0	3.0
12	2256.0	48.0	48.4	128.0	2.0
13	2210.3	45.7	52.4	127.0	1.0
14	2161.6	48.7	56.8	125.0	2.0
15	2108.8	52.8	61.5	123.0	2.0
16	2063.7	45.1	65.5	120.0	3.0
17	2021.7	42.0	69.2	118.0	2.0
18	1961.7	60.0	74.6	115.0	3.0
19	1915.0	46.7	78.7	113.0	2.0
20	1854.5	60.5	84.1	109.0	4.0

21	1824.7	29.8	86.8	103.0	6.0
22	1793.5	31.2	89.6	80.0	23.0
23	1744.1	49.4	94.0	0.0	80.0

TABLE 5A

Burst	Total Wt. (gms)	Weight Change (gms)	Discharge (%)	Pressure (psig)	Pressure Change (psig)
0	2863.8		-0.0	151.0	
1	2715.3	148.5	12.5	90.0	61.0
2	2601.9	113.4	22.1	70.0	20.0
3	2521.5	80.4	28.8	62.0	8.0
4	2446.7	74.8	35.1	56.0	6.0
5	2358.5	88.2	42.6	51.0	5.0
6	2271.2	87.3	49.9	46.0	5.0
7	2179.0	92.2	57.7	43.0	3.0
8	2065.2	113.8	67.3	39.0	4.0
9	1924.7	140.5	79.1	36.0	3.0
10	1812.6	112.1	88.5	30.0	6.0
11	1791.6	21.0	90.3	15.0	15.0

I claim:

1. A process for preventing, controlling and extinguishing fire in an enclosed air-containing, mammalian-habitable enclosed area which contains combustible materials of the non-self-sustaining type, which comprises introducing into the air in said enclosed area an amount of CHF_3 sufficient to impart a heat capacity per mol of total oxygen that will suppress combustion of the combustible materials in said enclosed area.

2. A process as in Claim 1 wherein make-up oxygen is also introduced into said enclosed area in an amount from zero to the amount required to provide, together with the oxygen present in said air, sufficient total oxygen to sustain mammalian life.

3. A process as in Claim 1 wherein the amount of CHF_3 in said enclosed area is maintained at a level of about 14 to 80 volume percent.

4. A process as in Claim 1 wherein the amount of CHF_3 in said enclosed area is maintained at about 24 volume percent.

5. A process as in Claim 1 wherein at least 1% of at least one halogenated hydrocarbon is blended with said CHF_3 introduced into said enclosed area, said halogenated hydrocarbon being selected from the group consisting of difluoromethane (HFC-32), chlorodifluorometha (HCFC-22), 2,2-dichloro-1,1,1-trifluoroethane HCFC-123), 1,2-dichloro-1,1,2-trifluoroethane (HCFC-123a), 2-chloro-1,1,1,2-tetrafluoroethane (HCFC-124), 1-chloro-1,1,2,2-tetrafluoroethane

(HCFC-124a), pentafluoroethane (HFC-125), 1,1,2,2-tetrafluoroethane (HFC-134), 1,1,1,2-tetrafluoroethane (HFC-134a), 3,3-dichloro-1,1,1,2,2-pentafluoropropane (HCFC-225ca), 1,3-dichloro-1,1,2,2,3-pentafluoropropane (HCFC-225cb), 2,2-dichloro-1,1,1,3,3-pentafluoropropane (HCFC-225aa), 2,3-dichloro1,1,1,3,3-pentafluoropropane (HCFC-225da), 1,1,1,2,2,3,3-heptafluoropropane (HFC-227ca), 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea), 1,1,1,2,3,3-hexafluoropropane (HFC-236ea), 1,1,1,3,3,3-hexafluoropropane (HFC-236fa), 1,1,1,2,2,3-hexafluoropropane (HFC-236cb), 1,1,2,2,3,3-hexafluoropropane (HFC-236ca), 3-chloro-1,1,2,2,3-pentafluoropropane (HCFC-235ca), 3-chloro-1,1,1,2,2-pentafluoropropane (HCFC-235cb), 1-chloro-1,1,2,2,3-pentafluoropropane (HCFC-235cc), 3-chloro-1,1,1,3,3-pentafluoropropane (HCFC-235fa), 3-chloro 1,1,1,2,2,3-hexafluoropropane (HCFC-226ca), 1-chloro-1,1,2,2,3,3-hexafluoropropane (HCFC-226cb), 2-chloro-1,1,1,3,3,3-hexafluoropropane (HCFC-226da), 3-chloro-1,1,1,2,3,3-hexafluoropropane (HCFC-226ea), and 2-chloro-1,1,1,2,3,3-hexafluoropropane (HCFC-226ba)

6. A process for extinguishing a fire which comprises introducing a volume of CHF_3 sufficient to provide an extinguishing concentration in an enclosed area, and maintaining said concentration at a value of less than 80 volume percent until said fire is extinguished.

7. A process as in Claim 6 wherein at least 1% of at least one halogenated hydrocarbon is blended with said CHF_3 introduced into said enclosed area, said halogenated hydrocarbon being selected from the group consisting of difluoromethane (HFC-32), chlorodifluoromethane (HCFC-22), 2,2-dichloro-1,1,1-trifluoroethane HCFC-123), 1,2-dichloro-1,1,2-trifluoroethane

(HCFC-123a), 2-chloro-1,1,1,2-tetrafluoroethane (HCFC-124), 1-chloro-1,1,2,2-tetrafluoroethane (HCFC-124a), pentafluoroethane (HFC-125), 1,1,2,2-tetrafluoroethane (HFC-134), 1,1,1,2-tetrafluoroethane (HFC-134a), 3,3-dichloro-1,1,1,2,2-pentafluoropropane (HCFC-225ca), 1,3-dichloro-1,1,2,2,3-pentafluoropropane (HCFC-225cb), 2,2-dichloro-1,1,1,3,3-pentafluoropropane (HCFC-225aa), 2,3-dichloro1,1,1,3,3-pentafluoropropane (HCFC-225da), 1,1,1,2,2,3,3-heptafluoropropane (HFC-227ca), 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea), 1,1,1,2,3,3-hexafluoropropane (HFC-236ea), 1,1,1,3,3,3-hexafluoropropane (HFC-236fa), 1,1,1,2,2,3-hexafluoropropane (HFC-236cb), 1,1,2,2,3,3-hexafluoropropane (HFC-236ca), 3-chloro-1,1,2,2,3-pentafluoropropane (HCFC-235ca), 3-chloro-1,1,1,2,2-pentafluoropropane (HCFC-235cb), 1-chloro-1,1,2,2,3-pentafluoropropane (HCFC-235cc), 3-chloro-1,1,1,3,3-pentafluoropropane (HCFC-235fa), 3-chloro 1,1,1,2,2,3-hexafluoropropane (HCFC-226ca), 1-chloro-1,1,2,2,3,3-hexafluoropropane (HCFC-226cb), 2-chloro-1,1,1,3,3,3-hexafluoropropane (HCFC-226da), 3-chloro-1,1,1,2,3,3-hexafluoropropane (HCFC-226ea), and 2-chloro-1,1,1,2,3,3-hexafluoropropane (HCFC-226ba)

8. A fire extinguishing composition of low toxicity comprising at least 14 volume percent of CHF_3.

9. The composition of Claim 8 wherein at least 1% of at least one halogenated hydrocarbon is blended with said CHF_3 introduced into said enclosed area, said halogenated hydrocarbon being selected from the group consisting of difluoromethane (HFC-32), chlorodifluoromethane (HCFC-22), 2,2-dichloro-1,1,1-trifluoroethane HCFC-123), 1,2-dichloro-1,1,2-trifluoroethane (HCFC-123a), 2-chloro-1,1,1,2-tetrafluoroethane (HCFC-124),

1-chloro-1,1,2,2-tetrafluoroethane (HCFC-124a), pentafluoroethane (HFC-125), 1,1,2,2-tetrafluoroethane (HFC-134), 1,1,1,2-tetrafluoroethane (HFC-134a), 3,3-dichloro-1,1,1,2,2-pentafluoropropane (HCFC-225ca), 1,3-dichloro-1,1,2,2,3-pentafluoropropane (HCFC-225cb), 2,2-dichloro-1,1,1,3,3-pentafluoropropane (HCFC-225aa), 2,3-dichlorol,1,1,3,3-pentafluoropropane (HCFC-225da), 1,1,1,2,2,3,3-heptafluoropropane (HFC-227ca), 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea), 1,1,1,2,3,3-hexafluoropropane (HFC-236ea), 1,1,1,3,3,3-hexafluoropropane (HFC-236fa), 1,1,1,2,2,3-hexafluoropropane (HFC-236cb), 1,1,2,2,3,3-hexafluoropropane (HFC-236ca), 3-chloro-1,1,2,2,3-pentafluoropropane (HCFC-235ca), 3-chloro-1,1,1,2,2-pentafluoropropane (HCFC-235cb), 1-chloro-1,1,2,2,3-pentafluoropropane (HCFC-235cc), 3-chloro-1,1,1,3,3-pentafluoropropane (HCFC-235fa), 3-chloro 1,1,1,2,2,3-hexafluoropropane (HCFC-226ca), 1-chloro-1,1,2,2,3,3-hexafluoropropane (HCFC-226cb), 2-chloro-1,1,1,3,3,3-hexafluoropropane (HCFC-226da), 3-chloro-1,1,1,2,3,3-hexafluoropropane (HCFC-226ea), and 2-chloro-1,1,1,2,3,3-hexafluoropropane (HCFC-226ba)

10. A propellant for fire extinguisher having tri-fluoromethane as the predominant component.

11. A process for extinguishing fire in an area which contains combustible materials, which comprises introducing into said area an amount of CHF_3 sufficient to suppress combustion of the combustible materials in said area.

12. A process as in Claim 1 wherein at least 1% of at least one halogenated hydrocarbon is blended with said CHF_3 introduced into said area, said halogenated hydrocarbon being selected from the group consisting of difluoromethane (HFC-32), chlorodifluoromethane (HCFC-22),

2,2-dichloro-1,1,1-trifluoroethane HCFC-123), 1,2-dichloro-1,1,2-trifluoroethane (HCFC-123a), 2-chloro-1,1,1,2-tetrafluoroethane (HCFC-124), 1-chloro-1,1,2,2-tetrafluoroethane (HCFC-124a), pentafluoroethane (HFC-125), 1,1,2,2-tetrafluoroethane (HFC-134), 1,1,1,2-tetrafluoroethane (HFC-134a), 3,3-dichloro-1,1,1,2,2-pentafluoropropane (HCFC-225ca), 1,3-dichloro-1,1,2,2,3-pentafluoropropane (HCFC-225cb), 2,2-dichloro-1,1,1,3,3-pentafluoropropane (HCFC-225aa), 2,3-dichloro1,1,1,3,3-pentafluoropropane (HCFC-225da), 1,1,1,2,2,3,3-heptafluoropropane (HFC-227ca), 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea), 1,1,1,2,3,3-hexafluoropropane (HFC-236ea), 1,1,1,3,3,3-hexafluoropropane (HFC-236fa), 1,1,1,2,2,3-hexafluoropropane (HFC-236cb), 1,1,2,2,3,3-hexafluoropropane (HFC-236ca), 3-chloro-1,1,2,2,3-pentafluoropropane (HCFC-235ca), 3-chloro-1,1,1,2,2-pentafluoropropane (HCFC-235cb), 1-chloro-1,1,2,2,3-pentafluoropropane (HCFC-235cc), 3-chloro-1,1,1,3,3-pentafluoropropane (HCFC-235fa), 3-chloro 1,1,1,2,2,3-hexafluoropropane (HCFC-226ca), 1-chloro-1,1,2,2,3,3-hexafluoropropane (HCFC-226cb), 2-chloro-1,1,1,3,3,3-hexafluoropropane (HCFC-226da), 3-chloro-1,1,1,2,3,3-hexafluoropropane (HCFC-226ea), and 2-chloro-1,1,1,2,3,3-hexafluoropropane (HCFC-226ba)

INTERNATIONAL SEARCH REPORT

International Application No PCT/US90/05506

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

INT. CL. 5: A62C 2/00
U.S.CLASS: 169/44

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
U.S.	169/43,44,45,46,47,54 252/2,3,601,603,605

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
Y	US, A, 4,807,706 (LAMBERTSEN ET AL) 28 February 1989 See the abstract.	1-9
Y	US, A, 4,446,923 (MARTIN) 08 May 1984 See column 1, paragraph 3.	1-9
Y	US, A, 4,233,177 (WITTENHORST) 11 November 1980 See the entire document.	5,7,9
A	US, A, 4,234,432 (TARPLEY, JR.) 18 November 1980	

* Special categories of cited documents: [15]
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2]	Date of Mailing of this International Search Report [2]
03 DECEMBER 1990	12 FEB 1991
International Searching Authority [1]	**Signature of Authorized Officer [20]**
ISA/US	S. P. AVILA